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(19) (CA) APPLICATION FOR CANADIAN PATENT (12)

(54) Organosilicon Compounds Having a Cage-Like Structure

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Notice: This application is as filed and may therefore contain an incomplete specification.



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ORGANOSILICON COMPOUNDS HAVING
A CAGE-LIKE STRUCTURE

Abstract of Disclosure

Organosilicon compounds of the formula

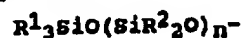


(I),

in which

z is 4, 6, 8, 10, 12 or 14, and

R can be identical or different and represents a hydrogen atom,
an organic radical or radicals of the formula



(II)

in which

R¹ can be identical or different and represents a hydrogen atom,
an organic radical or an organosilicon radical,

R² can be identical or different and represents a hydrogen atom
or an organic radical and

n is 0 or an integer,

with the proviso that the organosilicon compound of formula (I)
contains at least one radical R of formula (II) where n > 0.

ORGANOSILICON COMPOUNDS HAVING
A CAGE-LIKE STRUCTURE

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Field of Invention

The present invention relates to organosilicon compounds having a cage-like structure, processes for their preparation and their use.

Background of Invention

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Organosilicon compounds having a cage-like structure and processes for their preparation are already known. Reference may be made to DE 3,837,397 A1 (Wacker-Chemie GmbH; published on May 10, 1990) and corresponding U.S. 5,047,492 (issued on September 10th, 1991), P.A. Agaskar, Inorg. Chem. 29(9) (1990) 1603, P.A. Agaskar, V.W. Day and W. G. Klemperer, J. Am. Chem. Soc. 109 (1987) 5554-6, D. Hoebbel et al., Z. Chem. 22(2) (1989), 260 and I. Hasegawa, S. Sakka 328 (1989) 140.

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However, these compounds do not produce, or produce unsatisfactory homogeneous mixtures with organopolysiloxanes, resulting in disadvantages when these compounds are employed in silicone-containing compositions.

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Summary of Invention

The present invention relates to organosilicon compounds of the formula

25



in which

z is 4, 6, 8, 10, 12 or 14, preferably 6, 8 or 10, more preferably 8, and

R can be identical or different and represents a hydrogen atom, an organic radical or radicals of the formula

30

in which

R^1 can be identical or different and represents a hydrogen atom,
an organic radical or an organosilicon radical,

5 R^2 can be identical or different and represents a hydrogen atom
or an organic radical and

n is 0 or an integer, preferably 0 or an integer from 1 to 20,
more preferably 0 or an integer from 1 to 10,

10 with the proviso that the organosilicon compound of formula (I)
contains at least one radical R of formula (II) where $n > 0$.

The organosilicon compounds of formula (I) according to the
invention preferably contain more than one radical R of formula
(II) where $n > 0$. However, organosilicon compounds of formula (I)
wherein all the radicals represent radicals of formula (II),
15 wherein n is on an average of $1/z$ to 4, wherein z is as mentioned
above, are more preferred.

Preferably, in the radical R of formula (II), not more than
one radical R^1 represents a hydrogen atom.

In formula (II), R^1 represents an organosilicon radical of
20 formula



in which

R^3 and R^4 can be identical or different and

R^2 is the same as above and

25 m is 0 or an integer, preferably 0.

If R^1 represents an organosilicon radical of formula (III),
the radical R of formula (II) preferably contains at least two
radicals R^1 of the organosilicon radical of formula (III).

30 Preferably, in radical R^1 of formula (III), not more than one
radical R^3 represents a hydrogen atom.

Examples of substituted hydrocarbon radicals as an organic radical R are halogenated hydrocarbon radicals, such as the chloromethyl, 3-chloropropyl, 3-bromopropyl, 3,3,3-trifluoropropyl and 5,5,5,4,4,3,3-heptafluoropentyl radical and the perfluoro-hexyl-ethyl and the chlorophenyl, dichlorophenyl and trifluorotolyl radical; mercaptoalkyl radicals, such as the 2-mercaptoethyl and 3-mercaptopropyl radicals; cyanoalkyl radicals, such as the 2-cyanoethyl and 3-cyanopropyl radicals; acyloxyalkyl radicals, such as the 3-acryloxypropyl and 3-methacryloxypropyl radical, and hydroxyalkyl radicals, such as the hydroxypropyl radical.

Examples of radicals R of formula (II) are

$\text{Me}_3\text{SiO}(\text{SiPhMeO})_{0-4^-}$, $(\text{Me}_3\text{SiO})_2\text{MeSiOSiMe}_2\text{O}^-$,
 $(\text{ViMe}_2\text{SiO})_2\text{MeSiOSiMe}_2\text{O}^-$, $(\text{HMe}_2\text{SiO})_2\text{MeSiOSiMe}_2\text{O}^-$,
 $\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{HMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$,
 $\text{ViMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{Me}_3\text{SiO}(\text{SiHMeO})_{0-4^-}$,
 $\text{Me}_3\text{SiO}(\text{SiMeViO})_{0-4^-}$, $\text{ViMe}_2\text{SiO}(\text{SiMeViO})_{0-4^-}$,
 $\text{HMe}_2\text{SiO}(\text{SiHMeO})_{0-4^-}$, $\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiHMeO})]_{0-4^-}$,
 $\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiViMeO})]_{0-4^-}$, $(\text{Me}_3\text{SiO})_3\text{SiOSiMe}_2\text{O}^-$,
 $(\text{ViMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}^-$, $(\text{HMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}^-$ and
 $(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{Me}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $-(\text{SiMe}_2\text{O})_{1-5^-}$, $-(\text{SiViMeO})_{1-5^-}$,
 $-(\text{SiHMeO})_{1-5^-}$, $-(\text{SiPhMeO})_{1-5^-}$ and $-(\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{MeO})_{1-5^-}$,
 in which

Me represents the methyl radical,

Vi represents the vinyl radical and

Ph represents the phenyl radical.

The radical R of formula (II) is preferably

$\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{HMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{ViMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$,
 $\text{Me}_3\text{SiO}(\text{SiHMeO})_{0-4^-}$, $\text{Me}_3\text{SiO}(\text{SiMeViO})_{0-4^-}$, $\text{ViMe}_2\text{SiO}(\text{SiMeViO})_{0-4^-}$,
 $\text{HMe}_2\text{SiO}(\text{SiHMeO})_{0-4^-}$, $\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiHMeO})]_{0-4^-}$.

$\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiViMeO})]_{0-4^-}$, $(\text{Me}_3\text{SiO})_3\text{SiOSiMe}_2\text{O}-$,
 $(\text{ViMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}-$, $(\text{HMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}-$ and
 $(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{Me}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $-(\text{SiMe}_2\text{O})_{1-5^-}$, $-(\text{SiViMeO})_{1-5^-}$,
 $-(\text{SiHMeO})_{1-5^-}$, $-(\text{SiPhMeO})_{1-5^-}$ and $-(\text{Si}(\text{CH}_2\text{CH}_2\text{CF}_3)\text{MeO})_{1-5^-}$,
 5 where $\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{HMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$,
 $\text{ViMe}_2\text{SiO}(\text{SiMe}_2\text{O})_{0-4^-}$, $\text{Me}_3\text{SiO}(\text{SiHMeO})_{0-4^-}$, $\text{Me}_3\text{SiO}(\text{SiMeViO})_{0-4^-}$,
 $\text{ViMe}_2\text{SiO}(\text{SiMeViO})_{0-4^-}$, $\text{HMe}_2\text{SiO}(\text{SiHMeO})_{0-4^-}$,
 $\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiHMeO})]_{0-4^-}$, $\text{Me}_3\text{SiO}[(\text{SiMe}_2\text{O})/(\text{SiViMeO})]_{0-4^-}$,
 $(\text{ViMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}-$ and $(\text{HMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{O}-$ are more preferred
 10 and

Me represents the methyl radical,
 Vi represents the vinyl radical and
 Ph represents the phenyl radical.

15 R^1 is preferably a hydrogen atom or methyl, vinyl, 3-chloro-
 propyl or organosilicon radicals, the hydrogen atom and methyl,
 vinyl and organosilicon radicals being more preferred.

Examples of organic radicals R^1 are the examples given for R
 as an organic radical.

20 Examples of organosilicon radicals R^1 are the $\text{Me}_3\text{SiO}-$,
 $\text{ViSiMe}_2\text{O}-$, $\text{HSiMe}_2\text{O}-$ and $(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{SiMe}_2\text{O}-$ radical, and all
 the organosilicon radicals mentioned for the radical R, where the
 $\text{Me}_3\text{SiO}-$, $\text{ViSiMe}_2\text{O}-$ and $\text{HSiMe}_2\text{O}-$ and $(\text{ClCH}_2\text{CH}_2\text{CH}_2)\text{SiMe}_2\text{O}-$ radical
 are preferred and the $\text{Me}_3\text{SiO}-$, $\text{ViSiMe}_2\text{O}-$ and $\text{HSiMe}_2\text{O}-$ radical are
 more preferred, and where

25 Me is the methyl radical and
 Vi is the vinyl radical.

R^2 is preferably a hydrogen atom or the methyl, vinyl, phenyl
 or 3,3,3-trifluoropropyl radical, where a hydrogen atom and methyl
 . and vinyl radicals are more preferred.

Examples of organic radical R^2 are the examples given for the radical R as an organic radical.

R^3 is preferably a hydrogen atom or the methyl, vinyl or 3-chloropropyl radical, where a hydrogen atom and the methyl and vinyl radical are more preferred.

Examples of organic radicals R^3 are the examples given for the radical R as an organic radical.

R^4 is preferably a hydrogen atom or the methyl or vinyl radical, where the methyl radical is more preferred.

Examples of organic radicals R^4 are the examples given for the radical R as an organic radical.

Examples of the organosilicon compounds of formula (I) are

$[ViMe_2SiO(SiMe_2O)_nSiO_3/2]_z$, $[HMe_2SiO(SiMe_2O)_nSiO_3/2]_z$,
 $[Me_3SiO(SiViMeO)_nSiO_3/2]_z$, $[Me_3SiO(SiHMeO)_nSiO_3/2]_z$,
 $[ViMe_2SiO(SiViMeO)_nSiO_3/2]_z$, $[HMe_2SiO(SiHMeO)_nSiO_3/2]_z$,
 $[(ViMe_2SiO)_3SiOSiMe_2OSiO_3/2]_z$, $[(HMe_2SiO)_3SiOSiMe_2OSiO_3/2]_z$,
 $[(Me_3SiO)_3SiOSiMe_2OSiO_3/2]_z$, $[Me_3SiO(SiMe_2O)_nSiO_3/2]_z$
 $[Me_3SiO(SiPhMeO)_nSiO_3/2]_z$,
 $[Me_3SiO(Si(3,3,3-trifluoropropyl)MeO)_nSiO_3/2]_z$

$[(ClCH_2CH_2CH_2)Me_2SiO(SiMe_2O)_nSiO_3/2]_z$,
 $[(Me_3SiO)_2MeSiOSiMe_2OSiO_3/2]_z$, $[(ViMe_2SiO)_2MeSiOSiMe_2OSiO_3/2]_z$
and $[(HMe_2SiO)_2MeSiOSiMe_2OSiO_3/2]_z$, where

$[ViMe_2SiO(SiMe_2O)_nSiO_3/2]_z$, $[HMe_2SiO(SiMe_2O)_nSiO_3/2]_z$,
 $[Me_3SiO(SiViMeO)_nSiO_3/2]_z$, $[Me_3SiO(SiHMeO)_nSiO_3/2]_z$,
 $[ViMe_2SiO(SiViMeO)_nSiO_3/2]_z$, $[HMe_2SiO(SiHMeO)_nSiO_3/2]_z$,
 $[(ViMe_2SiO)_3SiOSiMe_2OSiO_3/2]_z$, $[(HMe_2SiO)_3SiOSiMe_2OSiO_3/2]_z$
 $[(Me_3SiO)_3SiOSiMe_2OSiO_3/2]_z$ and
 $[Me_3SiO(SiMe_2O)_nSiO_3/2]_z$ are preferred and

$[ViMe_2SiO(SiMe_2O)_nSiO_3/2]_z$, $[HMe_2SiO(SiMe_2O)_nSiO_3/2]_z$,
 $[Me_3SiO(SiViMeO)_nSiO_3/2]_z$, $[Me_3SiO(SiHMeO)_nSiO_3/2]_z$,
 $[ViMe_2SiO(SiViMeO)_nSiO_3/2]_z$, $[HMe_2SiO(SiHMeO)_nSiO_3/2]_z$,

$[(\text{ViMe}_2\text{SiO})_3\text{SiOSiMe}_2\text{OSiO}_3/2]_z$, and
 $[(\text{HMe}_2\text{SiO})_2\text{SiOSiMe}_2\text{OSiO}_3/2]_z$, are more preferred, and where

Me is the methyl radical,

Vi is the vinyl radical,

5 Ph is the phenyl radical,

z is 6, 8 or 10 and

n is on an average $1/z$ to 4.

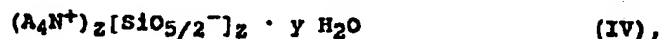
The organosilicon compounds of formula (I) have the advantage that they are miscible with liquid organopolysiloxanes. For example, the organosilicon compounds, as low-viscosity substances, are homogeneously miscible to an unlimited extent with medium-viscosity polydimethylsiloxane derivatives, e.g. those having a viscosity of up to 10,000 mPas, and up to 80% with more highly viscous substances.

15 Furthermore, the organosilicon compounds have the advantage that they have a high density of organofunctional radicals, such as, R^1 , R^2 , R^3 and R^4 , in groups of formula (II).

The organosilicon compounds of formula (I) can be prepared by various processes.

20 Process (1)

The present invention relates to a process for the preparation of the organosilicon compounds according to formula (I), which comprises reacting cage-like silicates of the formula



25 in which

y is a number between 50 and 300, preferably between 60 and 80,

z is the same as in formula (I) and

A can be identical or different and represents an alkyl radical, preferably an alkyl radical having 1 to 4 carbon atoms,

with at least one compound (A) of the formula



and/or a hydrolyzate or condensate thereof, in which

R^5 can be identical or different and is the same as R^2 above and

5 X represents a hydroxyl group, an organyloxy radical or a halogen atom,

and at least one organosilicon compound (B) chosen from the group comprising cyclic organopolysiloxanes of the formula



10 in which

R^6 can be identical or different and is the same as R^2 above and

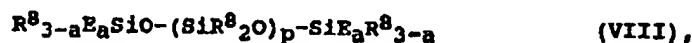
x represents 3 to 10, preferably 4 to 7, silanes of the formula



and/or partial hydrolyzates or condensates thereof, in which

R^7 can be identical or different and is the same as R^2 above and

20 D can be identical or different and is the same as X , and, organopolysiloxane of the formula



in which

R^8 can be identical or different and is the same as R^2 above,

a can be identical or different and represents 0 or 1,

25 p is 1 to 1,000, preferably 1 to 150, and

E can be identical or different and is the same as X above.

A silane of formula (VII) is preferably employed as component (B).

Process (1) can be carried out in the absence or presence of catalysts, preferably no catalyst being employed. If a catalyst is employed, acid catalysts are preferred, in particular hydrochloric acid.

5 Examples of acid catalysts are Lewis acids, such as AlCl_3 , BF_3 , TiCl_4 , SnCl_4 , SO_3 , PCl_5 , POCl_3 , FeCl_3 and hydrates thereof, ZnCl_2 , phosphonitrile chlorides, Brønsted acids, such as hydrochloric acid, hydrobromic acid, sulfuric acid, chlorosulfonic acid, phosphoric acid, o- and m-polyphosphoric acids, boric acid,
10 selenous acid, nitric acid, acetic acid, propionic acid, halogenoacetic acids, such as trichloro- or trifluoroacetic acid, oxalic acid and p-toluenesulfonic acid, acid ion exchangers, acid zeolites, acid-activated bleaching earth, hydrogen fluoride, hydrogen chloride and reactivated carbon black.

15 If a catalyst is employed in process (1) according to the invention, it is preferably used in amounts of 5% to 100% by weight, particularly preferably 10% to 50% by weight, based on the total weight of the silicate of formula (IV).

20 Process (1) is carried out at temperatures of preferably -10°C to 70°C , in particular 0°C to 40°C , under a pressure of preferably 800 to 2,000 hPa, particularly preferably 900 to 1,500 hPa.

25 Process (1) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvents.

 If solvents are used, solvents or solvent mixtures having a boiling point or boiling range of up to 120°C under 1,000 hPa are preferred.

30 Examples of such solvents are water, alcohols, such as methanol, ethanol, n-propanol and iso-propanol, ethers, such as

dioxane, tetrahydrofurane, diethyl ether and diethylene glycol dimethyl ether, chlorinated hydrocarbons, such as methylene-chloride, chloroform, carbon tetrachloride, 1,2-dichloroethane and trichloroethylene, hydrocarbons, such as pentane, n-hexane, hexane isomer mixtures, heptane, octane, wash benzine, petroleum ether, benzene, toluene and xylenes, ketones, such as acetone, methyl ethyl ketone and methyl isobutyl ketone, carbon disulphide and nitrobenzene, or mixtures of these solvents, with protic solvents, such as water, alcohols, such as methanol, ethanol, n-propanol and iso-propanol, and mixtures containing protic solvents being particularly preferred.

If a solvent is employed in process (1), it is preferably used in amounts of 200% to 3,000% by weight, particularly preferably 400% to 2,000% by weight, based on the total weight of silicate of formula (IV).

Preferably, in process (1), silicate of formula (IV) is added to a mixture of compound (A), compound (B), optionally a catalyst and solvent and the mixture is stirred for the desired reaction time. The phases are separated by addition of water and the organosilicon phase is washed neutral with water and freed from low-boiling constituents by distillation.

In process (1) component (A) is preferably employed in a molar ratio, based on the silicon atoms, of 1 to 30, more preferably 5 to 20, based on the silicon atoms in the silicate of formula (IV).

In process (1), component (B) is preferably employed in a molar ratio, based on the silicon atoms, of 0.5 to 30, more preferably 5 to 20, based on the silicon atoms in the silicate of formula (IV).

Preferably, X is a hydroxyl group, a chlorine atom or the ethoxy radical, where a chlorine atom is more preferred.

Compounds of formula (IV) are preferably

5 $(Me_4N^+)_8[SiO_5/2]_8 \cdot 69 H_2O$, $(Et_4N^+)_6[SiO_5/2]_6 \cdot 57 H_2O$ and $(Bu_4N^+)_{10}[SiO_5/2]_{10} \cdot 265 H_2O$, where $(Me_4N^+)_8[SiO_5/2]_8 \cdot 69 H_2O$ is more preferred and

Me represents the methyl radical,

Et represents the ethyl radical and

Bu represents the n-butyl radical.

10 Compounds of formula (IV) and processes for their preparation are already known. In this context, reference may be made to D. Hoebbel, W. Wieker, H. Jancke, G. Engelhard, Z.Chem. 14(3) (1974) 109, I. Hasegawa, S. Sakka, ACS Symp. Ser. 398 (1989) 140, D. Hoebbel, W. Wieker, Z. Allg. Anorg. Chem. 384 (1971) 43-52 and
15 I. Hasegawa, S. Sakka, J. Mol. Liq. 34 (1987) 307-315.

Compounds of formula (V) are hydrolyzates or condensates thereof and are preferably trimethylchlorosilane, dimethylchlorosilane, vinyltrimethylchlorosilane, 3-chloropropyltrimethylchlorosilane, trimethylhydroxysilane, vinyltrimethylhydroxysilane, trimethylethoxysilane, dimethylmethoxysilane, vinyltrimethylmethoxysilane, trimethylethoxysilane, dimethylethoxysilane, vinyltrimethylethoxysilane, allyltrimethylchlorosilane, hexamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, 1,3-divinyldisiloxane and 1,3-bis(3-chloropropyl)tetramethyldisiloxane, where trimethylchlorosilane, dimethylchlorosilane, vinyltrimethylchlorosilane, 3-chloropropyltrimethylchlorosilane, Hexamethyldisiloxane, 1,1,3,3-tetramethyldisiloxane, 1,3-divinyldisiloxane and 1,3-bis(3-chloropropyl)tetramethyldisiloxane are more preferred.

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The compound of formula (VI) are preferably hexamethylcyclo-
 trisiloxane, 1,3,5-trimethylcyclotrisiloxane, octamethylcyclo-
 tetrasiloxane, 1,3,5,7-tetramethylcyclotetrasiloxane,
 1,3,5,7-tetravinyltetramethylcyclotetrasiloxane and 1,3,5,7-tetra-
 (3,3,3-trifluoropropyl)tetramethylcyclotetrasiloxane, where octa-
 methylcyclotetrasiloxane is more preferred.

The compounds of formula (VII) are preferably dimethyldi-
 chlorosilane, methyldichlorosilane, vinylmethyldichlorosilane,
 dimethyldimethoxysilane, methyldimethoxysilane, vinylmethyldi-
 methoxysilane, dimethyldiethoxysilane, methyldiethoxysilane and
 vinylmethyldiethoxysilane, where dimethyldichlorosilane is more
 preferred.

The compounds of formula (VIII) are preferably α, w -dihydroxy-
 polyphenylmethylsiloxanes, α, w -dihydroxy-polydiphenylsiloxanes,
 α -trimethylsiloxy- w -hydroxy-polydimethylsiloxanes, α -vinyl-di-
 methylsiloxy- w -hydroxy-polydimethylsiloxanes, α, w -dihydroxypoly-
 dimethylsiloxanes, α, w -di(dimethyl-3-chloropropylsiloxy)polydi-
 methylsiloxanes, α, w -di(trimethylsiloxy)polydimethylsiloxanes,
 α, w -di(dimethylHsiloxy)polydimethylsiloxanes, α, w -di(dimethyl-
 vinylsiloxy)polydimethylsiloxanes, α, w -dihydroxy-polyvinylmethyl-
 siloxanes, α, w -di(trimethylsiloxy)polyvinylmethylsiloxanes,
 α, w -di(dimethylvinylsiloxy)polyvinylmethylsiloxanes, α, w -dihy-
 droxypoly(vinylmethyl/dimethyl)siloxanes, α, w -di(trimethylsiloxy)-
 poly(vinylmethyl/dimethyl)siloxanes, α, w -di(dimethylvinylsiloxy)-
 poly(vinylmethyl/dimethyl)siloxanes, α, w -di(dimethylHsiloxy)poly-
 methylHsiloxy, α, w -di(trimethylsiloxy)polymethylHsiloxy,
 α, w -di(trimethylsiloxy)polymethylH/dimethylsiloxanes
 and α, w -di(dimethylHsiloxy)poly(methylH/dimethyl)siloxane, where
 α, w -dihydroxy-polydimethylsiloxanes, α, w -di(trimethylsiloxy)poly-
 dimethylsiloxanes, α, w -di(dimethylHsiloxy)polydimethylsiloxanes,

5 α, ω -di(dimethylvinylsiloxypolydimethylsiloxanes, α, ω -dihydroxy-
 polyvinylmethylsiloxanes, α, ω -di(trimethylsiloxypolyvinylmethyl-
 siloxanes, α, ω -di(dimethylvinylsiloxypolyvinylmethylsiloxanes,
 α, ω -dihydroxy-poly(vinylmethyl/dimethyl)siloxanes, α, ω -di(tri-
 methylsiloxypoly(vinylmethyl/dimethyl)siloxanes, α, ω -di(dimethyl-
 vinylsiloxypoly(vinylmethyl/dimethyl)siloxanes, α, ω -di(dimethylH-
 siloxypolymethylHsiloxane, α, ω -di(trimethylsiloxypolymethylH-
 siloxane, α, ω -di(trimethylsiloxypoly(methylH/dimethyl)siloxanes,
 10 α, ω -di(dimethylHsiloxypoly(methylH/dimethyl)siloxanes are more
 preferred.

The compounds of formula (VIII) and mixtures thereof prefer-
 ably have a viscosity of 0.5 to 400 mPa·s at 25°C.

15 Process (1) has the advantage that the organosilicon com-
 pounds can be prepared in a simple manner and at a high rate of
 reaction. Process (1) furthermore has the advantage that it
 proceeds as a one-stage synthesis without significant side reac-
 tions. It moreover has the advantage that the reaction components
 are readily available.

Process (2)

20 The present invention further relates to a process for the
 preparation of the organosilicon compounds of formula (I) which
 comprises reacting organosilicon compounds of the formula



in which

25 R^9 can be identical or different and is the same as R^2 above
 and

z is the same as in formula (I) above,
 with at least one organosilicon compound (B) chosen from the group
 comprising compounds of formulas (VI), (VII) and (VIII) and
 30 optionally at least one compound (A) of formula (V) and/or a
 hydrolyzate or condensate thereof.

Compound (A) of formula (V) and/or a hydrolyzate or condensate thereof is preferably employed in process (2) according to the invention.

5 Examples of and preferred and more preferred compounds of formula (V) are those mentioned above under process (1).

Examples of and preferred and more preferred compounds of formula (VI) are those mentioned above under process (1).

Examples of and preferred and more preferred compounds of formula (VII) are those mentioned above under process (1).

10 Examples of and preferred and more preferred compounds of formula (VIII) are those mentioned above under process (1).

The compounds of formula (IX) are preferably $(\text{Me}_3\text{SiOSiO}_3/2)_6$, $(\text{Me}_3\text{SiOSiO}_3/2)_8$, $(\text{Me}_3\text{SiOSiO}_3/2)_{10}$, $(\text{HMe}_2\text{SiOSiO}_3/2)_6$, $(\text{HMe}_2\text{SiOSiO}_3/2)_8$, $(\text{HMe}_2\text{SiOSiO}_3/2)_{10}$, $(\text{ViMe}_2\text{SiOSiO}_3/2)_6$, $(\text{ViMe}_2\text{SiOSiO}_3/2)_8$, $(\text{ViMe}_2\text{SiOSiO}_3/2)_{10}$, $(\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiOSiO}_3/2)_6$, $(\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiOSiO}_3/2)_8$, and $(\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiOSiO}_3/2)_{10}$, where $(\text{Me}_3\text{SiOSiO}_3/2)_8$, $(\text{HMe}_2\text{SiOSiO}_3/2)_8$ and $(\text{ViMe}_2\text{SiOSiO}_3/2)_8$ are more preferred and Me represents the methyl radical and

20 Vi represents the vinyl radical.

Processes for the preparation of compounds of formula (IX) are already known. Reference may be made to the already mentioned DE 3,837,397 A1 and EP 348,705 (D. Hoebbel; published on January 3, 1990).

25 A compound of formula (VIII) is preferably employed as component (B).

Process (2) is preferably carried out in the presence of catalysts. The examples of catalysts given for process (1) also apply in their full scope to process (2) according to the invention.

30

Phosphonitrile chlorides, hydrochloric acid, acid ion exchangers, acid zeolites and acid-activated bleaching earth are preferably employed as the catalysts in process (2) with phosphonitrile chlorides being more preferred.

5 If a catalyst is employed in process (2), it is preferably used in amounts of 0.1% to 20% by weight, more preferably 0.3% to 10% by weight, based on the total weight of organosilicon compound of formula (IX).

10 Process (2) is carried out at temperatures of preferably -20°C to 200°C, in particular 20°C to 100°C, under a pressure of preferably 800 to 2,000 hPa, more preferably 900 to 1,500 hPa.

Process (2) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvents.

15 Examples of solvents employed, optionally, in process (2) are the examples of solvents given for process (1).

20 If a solvent is employed in process (2), it is preferably used in amounts of 200% to 3,000% by weight, more preferably 400% to 2,000% by weight, based on the total weight of organosilicon compound of formula (IX).

25 Preferably, in process (2), all the components are mixed with one another in any desired sequence and the mixture is stirred for the desired reaction time. Any catalyst is then deactivated with a basic compound, such as magnesium oxide, and, if a solvent has been employed, the phases are separated by addition of water. The organosilicon phase is washed neutral with water and freed from low-boiling constituents by distillation.

30 In process (2), component (A) is preferably employed in a molar ratio, based on the silicon atoms, of 1 to 30, more preferably 5 to 20, based on the silicon atoms in the $\text{SiO}_{3/2}$ units of the organosilicon compound of formula (IX).

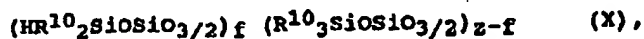
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In process (2), component (B) is preferably employed in a molar ratio, based on the silicon atoms, of 1 to 30, more preferably 5 to 20, based on the silicon atoms in the $\text{SiO}_{3/2}$ units of the organosilicon compound of formula (IX).

Process (2) has the advantage that the compounds can be prepared easily and in a high purity. The reaction is easy to control and proceeds selectively.

Process (3)

The present invention relates to a process for the preparation of the organosilicon compounds of formula (I), which comprises reacting organosilicon compounds of the formula



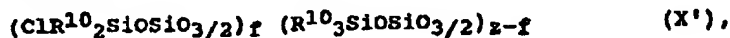
in which

R^{10} can be identical or different and is the same as R^2 above,

z is the same as in formula (I) and

f represents an integer from 1 to z ,

with allyl chloride in the presence of platinum metals and/or compounds thereof in a first stage to give the corresponding chlorine compounds of the formula



in which R^{10} , f and z are the same as mentioned above, and then reacting compounds of formula (X') in a second stage with at least one organosilicon compound (C) selected from the group consisting of silanes of the formula



in which R^{11} can be identical or different and is the same as R^2 above,

organopolysiloxanes of the formula



in which R^{12} can be identical or different and is the same as R^2 above and r represents 0 or an integer from 1 to 10,
organopolysiloxanes of the formula



5 in which R^{12} and r are the same as above and
organopolysiloxanes of the formula



in which R^{12} and r are the same as above.

10 The compounds of formula (XI) are preferably the hydroxy-silanes mentioned above for the compound of formula (V) where trimethylhydroxysilane and vinyl dimethylhydroxysilane are more preferred.

15 The organopolysiloxanes of formula (XII) are preferably the siloxanes having an Si-bonded hydroxyl group mentioned for compounds of formula (VIII), more preferably hydroxy-pentamethyldisiloxane, 1-hydroxy-3-vinyl-tetramethyldisiloxane, 1-hydroxy-3-hydrido-tetramethyldisiloxane and 1-hydroxy-7-vinyl-octamethyl-tetrasiloxane.

20 The organopolysiloxanes of formula (XIII) are preferably bis(trimethylsiloxy)methylhydroxysilane, bis(dimethylsiloxy)-methylhydroxysilane and bis(vinyl dimethylsiloxy)methylhydroxysilane, where bis(vinyl dimethylsiloxy)methylhydroxysilane is more preferred.

25 The organopolysiloxanes of formula (XIV) are preferably tris-(trimethylsiloxy)hydroxysilane, tris(dimethylsiloxy)hydroxysilane and tris(vinyl dimethylsiloxy)hydroxysilane, where tris(vinyl dimethylsiloxy)hydroxysilane is more preferred.

Organopolysiloxanes of formula (XIV) are preferably employed as compound (C).

Process (3) is preferably carried out under an inert gas such as nitrogen or argon.

Processes for the preparation of compound of formula (IX) are already known. Reference may be made to the above mentioned DE 3,837,397 A1 (Wacker-Chemie GmbH; published on May 10, 1990) and corresponding U.S. 5,047,492 (issued on September 10, 1991) and also EP 348,705 (D. Hoebebel; published on January 3, 1990).

Examples of the platinum metals and/or compounds thereof employed in the first stage of process (3) are very finely divided platinum metals, such as platinum, palladium, rhodium and iridium, platinum metals on supports such as silicon dioxide, aluminum oxide or active charcoal, platinum metal complexes which are bonded and soluble in hydrocarbons, such as PtCl_4 , $\text{NaPtCl}_4 \cdot 4\text{H}_2\text{O}$, platinum-olefin complexes, platinum-alcohol complexes, platinum-alcoholate complexes, platinum-ether complexes, platinum-aldehyde complexes, platinum-ketone complexes, platinum-vinylsiloxane complexes and dicyclopentadieneplatinum dichloride, with palladium/active charcoal, palladium diacetylacetonate and tris(tri-phenylphosphine)rhodium(I) chloride being preferred and palladium/active charcoal being more preferred.

The platinum catalyst is preferably employed in amounts of 50 to 400 ppm by weight (parts by weight per million parts by weight), in particular 100 to 300 ppm by weight, calculated as elemental platinum metal and based on the total weight of organo-silicon compound of formula (X).

The allyl chloride is preferably employed in a molar ratio of 1.0 to 5, in particular 1.0 to 2, per mol of Si-bonded hydrogen in the organosilicon compound of formula (X).

The first stage of process (3) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvent.

5 Examples of the solvents employed, optionally, in the first stage of process (3) according to the invention are the examples of solvents given for process (1), where aprotic solvents or solvent mixtures having a boiling point of up to 120°C under a pressure of 1,000 hPa are preferred.

10 If a solvent is employed in the first stage of process (3), it is preferably used in amounts of 100% to 2,000% by weight, more preferably 200 to 1,000% by weight, based on the total weight of organosilicon compound of formula (X).

15 The first stage of process (3) is carried out at temperatures of preferably 20°C to 50°C, in particular at the boiling point of allyl chloride, (45°C), under a pressure of preferably 800 to 2,000 hPa, more preferably 900 to 1,500 hPa.

20 After the first stage, the compound of formula (X') is reacted with compound (C) in a second stage, preferably with substantial exclusion of moisture and optionally in the presence of an acid-trapping agent.

25 In the second stage of process (3) component (C) is preferably employed in a molar ration, based on Si-bonded hydroxyl groups, of 1.0 to 1.5, more preferably 1.0 to 1.2, per mole of Si-bonded chlorine atom in the organosilicon compound of formula (X').

30 Acid-trapping agents which can be employed are compounds containing basic nitrogen, such as primary, secondary and tertiary amines and urea derivatives. The acid-trapping agent employed is preferably triethylamine, pyridine, 1,9-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,5-diazabicyclo[3.3.0]octane (DABCO), urea, tetra-

methyllurea, N,N'-dimethylurea, N,N'-dimethylpropyleneurea (DMPH) and bis(trimethylsilyl)urea (BSU), where triethylamine, pyridine and tetramethylurea are more preferred.

5 If an acid-trapping agent is employed in the second stage of process (3), it is preferably used in molar ratios of 1.0 to 1.1, more preferably 1.0, per mole of Si-bonded chlorine atoms in the organosilicon compound of formula (X').

10 The second stage of process (3) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvents.

Examples of the solvents employed, optionally, in the second stage of process (3) are the examples given above for the first stage.

15 If a solvent is employed in the second stage of process (3), it is preferably used in amounts of 200% to 3,000% by weight, more preferably 500% to 2,000% by weight, based on the total weight of organosilicon compound of formula (X').

20 The second stage of process (3) is carried out at temperatures of preferably 20°C to 120°C, in particular 30°C to 60°C, under a pressure of preferably 800 to 2,000 hPa, more preferably 900 to 1,500 hPa.

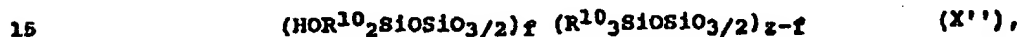
25 In a preferred embodiment of process (3), allyl chloride is added dropwise under an inert gas to a mixture of compound of formula (X), catalyst and, optionally, solvent and the mixture is stirred. When the first stage has ended, the reaction mixture is added under an inert gas to compound (C), as a mixture with an acid-trapping agent and solvent, and the mixture is stirred. When the second stage has ended, the catalyst and the organic chlorides are removed. The product is freed from solvent by distillation.

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Process (3) has the advantage that the compound of formula (I) prepared according to the invention is precisely defined and is not a mixture of different compounds of formula (I). Process (3) furthermore has the advantage that compound of formula (I) which have an extremely high density of organofunctional radicals, such as R^1 , R^2 , R^3 and R^4 , in groups of formula (II) can be prepared by the process.

Process (4)

The present invention further relates to a process for the preparation of the organosilicon compounds of formula (I) which comprises reacting organosilicon compounds of formula (X) with water in a first stage in the presence of platinum metals and/or compounds thereof to give the corresponding hydroxyl compounds of the formula



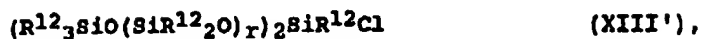
in which R^{10} , f and z are the same as above, and then reacting compounds of formula (X'') in a second stage with at least one organosilicon compound (C) chosen from the group comprising silanes of the formula



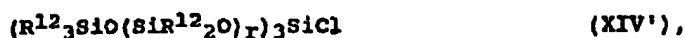
in which R^{11} can be identical or different and is the same as R^2 above, organopolysiloxanes of the formula



in which R^{12} can be identical or different and is the same as R^2 above and r represents 0 or an integer from 1 to 10, organopolysiloxanes of formula



in which R^{12} and r are the same as above, and
organopolysiloxanes of the formula



5 in which R^{12} and r are the same as above.

The compounds of formula (XI') are preferably the chlorosilanes mentioned above for the compound of formula (V) where trimethylchlorosilane, dimethylchlorosilane, vinyltrimethylchlorosilane and 3-chloropropyltrimethylchlorosilane are more preferred.

10 The organopolysiloxanes of formula (XII') are preferably the siloxanes having an Si-bonded chlorine atom mentioned for compounds of formula (VIII), more preferably chloropentamethyldisiloxane, 1-chloro-3-vinyl-tetramethyldisiloxane, 1-chloro-3-hydridotetramethyldisiloxane and 1-chloro-7-vinyl-octamethyltetrasiloxane.

15 The organopolysiloxanes of formula (XIII') are preferably bis(trimethylsiloxy)methylchlorosilane, bis(dimethylsiloxy)methylchlorosilane and bis(vinyltrimethylsiloxy)methylchlorosilane, where bis(vinyltrimethylsiloxy)methylchlorosilane is more preferred.

20 The organopolysiloxanes of formula (XIV') are preferably tris(trimethylsiloxy)chlorosilane, tris(dimethylsiloxy)chlorosilane and tris(vinyltrimethylsiloxy)chlorosilane, where tris(vinyltrimethylsiloxy)chlorosilane is more preferred.

25 Organosilicon compounds of formulas (XI'), (XII') and (XIV') are preferably employed as compound (C), more preferably compounds of formula (XIV').

Process (4) according to the invention is preferably carried out under an inert gas, such as nitrogen or argon.

Examples of the platinum metals and/or compounds thereof employed in the first stage of process (4) are the examples given in process (3), where platinum/active charcoal, platinum-olefin complexes, such as those with 1-octene, cyclopentadiene and norbornadiene, and platinum-vinylsiloxane complexes, such as those with divinyltetramethyldisiloxane, are preferred and palladium/active charcoal is more preferred.

The platinum catalyst is preferably employed in amounts of 50 to 400 ppm by weight (parts by weight per million parts by weight), in particular 100 to 300 ppm by weight, calculated as elemental platinum metal and based on the total weight of the organosilicon compound of formula (X).

Water is preferably employed in molar ratios of 1.0 to 1.3, in particular 1.0 to 1.1, per mole of Si-bonded hydrogen in the organosilicon compound of formula (X).

The first stage of process (4) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvents.

Examples of the solvents employed, optionally, in the first stage of process (4) are the examples of solvents given for process (3), where polar-aprotic solvents or solvent mixtures having a boiling point of up to 120°C under a pressure of 1,000 hPa are preferred.

If a solvent is employed in the first stage of process (4), it is preferably used in amounts of 100% to 2,000% by weight, more preferably 200% to 1,000% by weight, based on the total weight of organosilicon compound of formula (X).

The first stage of process (4) is carried out at temperatures of preferably 20°C to 100°C, in particular 40°C to 80°C, under a

pressure of preferably 800 to 2,000 hPa, more preferably 900 to 1,500 hPa.

5 After the first stage, the compound of formula (X'') is reacted with compound (C) in a second stage, optionally in the presence of an acid-trapping agent, where this second stage is preferably carried out such that no moisture is involved.

10 In the second stage of process (4), component (C) is preferably employed in molar ratios of 1.0 to 1.5, more preferably 1.0 to 1.2, per mole of Si-bonded hydroxyl groups in the organosilicon compound of formula (X'').

The acid-trapping agents are the acid-trapping agents described above in process (3).

15 If an acid-trapping agent is employed in the second stage of process (4), it is preferably used in molar ratios of 1.0 to 1.1, more preferably 1.0, per mole of Si-bonded chlorine atoms in the organosilicon compound of formula (X'').

The second stage of process (4) can be carried out in the presence or in the absence of solvents, and is preferably carried out in the presence of solvents.

20 Examples of the solvents employed, optionally, in the second stage of process (4) are the examples given above for the first stage of process (3).

25 If a solvent is employed in the second stage of process (4), it is preferably used in amounts of 200% to 3,000% by weight, more preferably 500% to 2,000% by weight, based on the total weight of organosilicon compound of formula (X'').

30 The second stage of process (4) is carried out at temperatures of preferably 20°C to 120°C, in particular 30°C to 60°C, under a pressure of preferably 800 to 2,000 hPa, more preferably 900 to 1,500 hPa.

In a preferred embodiment of process (4), a compound of formula (X), water, catalyst and optionally solvent are stirred with one another under an inert gas. When the first stage has ended, the reaction mixture is added under an inert gas to compound (C), as a mixture with acid-trapping agent and solvent, and the mixture is stirred. When the second stage has ended, the catalyst and the organic chlorides are removed. The product is freed from solvent by distillation.

Process (4) has the advantage that the compound of formula (I) prepared according to the invention is precisely defined and is not a mixture of different compounds of formula (I). Process (4) also has the advantage that compounds of formula (I) which have an extremely high density of organofunctional radicals, such as R^1 , R^2 , R^3 and R^4 in groups of formula (II) can be prepared by the process.

The organosilicon compounds and the organosilicon compounds prepared can be employed for all those purposes for which organosilicon compounds having a cage-like structure have also been used to date. In particular, they are suitable as cross-linking agents in silicone rubber compositions and resins, as initiators for polymerizations, as plasticizers, fillers, release agents and adhesion promoters, generally as surface-active substances for polymers, in particular for organopolysiloxanes because of their good solubility, and as a standard for spectroscopic and chromatographic analytical methods.

In the examples described below, all the data on parts and percentages relate to the weight, unless stated otherwise. Furthermore, all the viscosity data are based on a temperature of

25°C. Unless stated otherwise, the following examples were carried out under a pressure of the surrounding atmosphere of about 1,000 hPa, and at room temperature at about 20°C, or at a temperature which is established when the reactants are brought together at room temperature without additional heating or cooling.

Abbreviations used in the following examples are:

Me for the methyl radical and

Vi for the vinyl radical

Example 1

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasilicate and 4 g of water) are added in portions to a well-stirred mixture of 100 ml of isopropanol, 70 ml of toluene, 8.9 ml of trimethylchlorosilane and 23 ml of dimethyldichlorosilane at a temperature of 0°C and the mixture is stirred for 1 hour. A further 17.8 ml of trimethylchlorosilane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. The excess silane is then hydrolyzed with ice-water and the phases are separated. The organic phase is washed until neutral and dried over Na_2SO_4 and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.4 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiO}_3/2]_8$ in which n is on average 1.4, are obtained.

Example 2

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasili-

cate and 4 g of water) are added in portions to a well-stirred mixture of 100 ml of isopropanol, 70 ml of toluene, 9.5 ml of vinyltrimethylchlorosilane and 23 ml of dimethyldichlorosilane at a temperature of 0°C and the mixture is stirred for 1 hour. A further 19 ml of vinyltrimethylchlorosilane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. The excess silane is then hydrolyzed with ice-water and the phases are separated. The organic phase is washed until neutral and dried over Na_2SO_4 and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.5 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{ViMe}_2\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiO}_{3/2}]_8$ in which n is on average 1.5, are obtained.

Example 3

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasilicate and 4 g of water) are added in portions to a well-stirred mixture of 7 ml of concentrated HCl , 100 ml of isopropanol, 70 ml of toluene, 6.2 ml of 1,1,3,3-tetramethyldisiloxane and 14.7 ml of octamethylcyclotetrasiloxane at a temperature of 0°C and the mixture is stirred for 1 hour. A further 12.4 ml of 1,1,3,3-tetramethyldisiloxane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. The excess silane is then hydrolyzed with ice-water and the phases are separated. The organic phase is washed until neutral and dried over Na_2SO_4 and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.1 g of a viscous substance

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having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{HMe}_2\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiO}_3/2]_8$ in which n is on average 1.3, are obtained.

5 **Example 4**

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasilicate and 4 g of water) are added in portions to a well-stirred mixture of 100 ml of isopropanol, 70 ml of toluene, 9.5 ml of vinyltrimethylchlorosilane and 24.6 ml of vinylmethyldichlorosilane at a temperature of 0°C and the mixture is stirred for 1 hour. A further 19 ml of vinyltrimethylchlorosilane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. The excess silane is then hydrolyzed with ice-water and the phases are separated. The organic phase is washed until neutral and dried over Na_2SO_4 and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.8 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{ViMe}_2\text{SiO}(\text{SiViMeO})_n\text{SiO}_3/2]_8$ in which n is on average 1.6, are obtained.

Example 5

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasilicate and 4 g of water) are added in portions to a well-stirred mixture of 7 ml concentrated HCl, 100 ml of isopropanol, 70 ml of toluene, 7.5 ml of hexamethyldisiloxane and 14.7 ml of 1,3,5,7-tetramethylcyclotetrasiloxane at a temperature of 0°C and the mixture is stirred for 1 hour. A

further 14.9 ml of hexamethyldisiloxane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. Water is added and the phases are separated. The organic phase is washed until neutral and dried over Na₂SO₄ and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.1 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{SiHMeO})_n\text{SiO}_3/2]_8$ in which n is on average 1.4, are obtained.

Example 6

10 g of a moist silicate of the formula $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasilicate and 4 g of water) are added in portions to a well-stirred mixture of 100 ml of isopropanol, 70 ml of toluene, 11.5 ml of 3-chloropropyldimethylchlorosilane and 23 ml of dimethyldichlorosilane at a temperature of 0°C and the mixture is stirred for 1 hour. A further 23 ml of 3-chloropropyldimethylchlorosilane are then added at a temperature of 0°C and the mixture is stirred for 20 minutes. The excess silane is then hydrolyzed with ice-water and the phases are separated. The organic phase is washed until neutral and dried over Na₂SO₄ and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 5.3 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Me}_2\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiO}_3/2]_8$ in which n is on average 1.6, are obtained.

Example 7

10 g of a moist silicate of the formula
 $(\text{Me}_4\text{N}^+)_8[\text{SiO}_5/2]_8 \cdot 69 \text{ H}_2\text{O}$ (corresponds to 6 g of octasili-
 cate and 4 g of water) are added in portions to a well-
 stirred mixture of 100 ml of isopropanol, 70 ml of toluene,
 7.6 ml of dimethylhydriochlorosilane and 19.8 ml of methyl-
 hydriodichlorosilane at a temperature of 0°C and the mixture
 is stirred for 1 hour. A further 15.3 ml of dimethylhydri-
 ochlorosilane are then added at a temperature of 0°C and the
 mixture is stirred for 20 minutes. The excess silane is then
 hydrolyzed with ice-water and the phases are separated. The
 organic phase is washed until neutral and dried over Na_2SO_4
 and the solvent and low-boiling siloxanes are removed by
 distillation at a temperature of 180°C under 1 Pa. 4.1 g of a
 viscous substance having a very narrow molecular weight
 distribution, according to the GPC diagram, and the structure
 $[\text{HMe}_2\text{SiO}(\text{SiHMeO})_n\text{SiO}_3/2]_8$ in which n is on average 1.2, are
 obtained.

Example 8

2.8 g of the octa(trimethylsiloxy)octasilsesquioxane
 $[(\text{CH}_3)_3\text{SiOSiO}_3/2]_8$ are stirred together with 1 ml of concen-
 trated HCl, 5.3 ml of hexamethyldisiloxane and 16.7 ml of
 α,ω -dihydroxypolyvinylmethylsiloxane having on average 150
 siloxy units as a heterogeneous reaction mixture at a temper-
 ature of 70°C for 24 hours. A further 15 ml of hexamethyldi-
 siloxane are then added and the mixture is then stirred at
 70°C for 2 hours. Water is added and the phases are
 separated. The organic phase is washed until neutral and
 dried over Na_2SO_4 and the solvent and low-boiling siloxanes
 are removed by distillation at a temperature of 180°C under

1 Pa. 4.5 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{Si}(\text{Me})\text{MeO})_n\text{SiO}_3/2]_8$ in which n is on average 1.5, are obtained.

5 **Example 9**

2.8 g of the octa(trimethylsiloxy)octasilsesquioxane $[(\text{CH}_3)_3\text{SiOSiO}_3/2]_8$ are dissolved in 30 ml of toluene together with 1 ml of concentrated HCl, 4.6 ml of hexamethyldisiloxane and 14 ml of α,ω -di(trimethylsilyl)polymethylhydridosiloxane having on average 60 siloxy units and the solution is stirred at a temperature of 70°C for 24 hours. A further 15 ml of hexamethyldisiloxane are then added and the mixture is then stirred at 70°C for 2 hours. Water is added and the phases are separated. The organic phase is washed until neutral and dried over Na_2SO_4 and the solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{SiHMeO})_n\text{SiO}_3/2]_8$ in which n is on average 1.3, are obtained.

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Example 10

2.8 g of the octa(trimethylsiloxy)octasilsesquioxane $[(\text{CH}_3)_3\text{SiOSiO}_3/2]_8$ are dissolved in 30 ml of toluene together with 0.08 ml of a 27% strength phosphonitrile chloride solution in ethyl acetate, 4.3 ml of hexamethyldisiloxane and 15.3 ml of α,ω -di(trimethylsilyl)poly(methylhydrido/dimethyl)siloxane having on average 35 siloxy units and a ratio of dimethylsiloxy units to methylhydrido units of 1:1 and the

25

solution is stirred at a temperature of 70°C for 24 hours. A further 14.9 ml of hexamethyldisiloxane are then added and the mixture is then stirred at 70°C for 2 hours. The catalyst is then deactivated with magnesium oxide, and solids are then filtered off. The solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.1 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{SiHMeO})_m(\text{SiMe}_2\text{O})_n\text{SiO}_3/2]_8$ in which m is on average 0.7 and n is on average 0.7, are obtained.

Example 11

2.8 g of the deca(trimethylsiloxy)decasilsesquioxane $[(\text{CH}_3)_3\text{SiOSiO}_3/2]_{10}$ are dissolved in 30 ml of toluene together with 0.08 ml of a 27% strength phosphonitrile chloride solution in ethyl acetate, 4.7 ml of hexamethyldisiloxane and 17 ml of α,ω -di(trimethylsilyl)polydimethylsiloxane having on average 65 siloxy units and the solution is stirred at a temperature of 70°C for 24 hours. A further 14.9 ml of hexamethyldisiloxane are then added and the mixture is then stirred at 70°C for 2 hours. The catalyst is then deactivated with magnesium oxide, and solids are then filtered off. The solvent and low-boiling siloxanes are removed by distillation at a temperature of 180°C under 1 Pa. 4.5 g of a viscous substance having a very narrow molecular weight distribution, according to the GPC diagram, and the structure $[\text{Me}_3\text{SiO}(\text{SiMe}_2\text{O})_n\text{SiO}_3/2]_{10}$ in which n is on average 1.4, are obtained.

Example 12

Reaction of octa(dimethylsiloxy)octasilsesquioxane acid $(\text{HSiMe}_2\text{OSiO}_3/2)_8$ with allyl chloride/palladium and

bis(trimethylsilyloxy)methylhydroxysilane.

2.5 ml of allyl chloride (30 mmol) are added dropwise, under nitrogen as an inert gas, to a well-stirred mixture of 2.5 g of octa(dimethylsiloxy)octasilsesquioxane (20 mmol of Si as the Q unit or as the M^H unit), 0.05 g of palladium (on active charcoal, 5%) and 8 ml of toluene at a temperature of 95°C and the mixture is stirred for 4 hours.

After cooling to room temperature, the reaction mixture is added, under an inert gas, to a well-stirred mixture of 4.9 g of bis(trimethylsilyloxy)methylhydroxysilane (20 mmol of Si as the T^{OH} unit), 3.1 ml of triethylamine (22 mmol) and 25 ml of toluene at a temperature of 50°C and the mixture is stirred for 1 hours.

The catalyst and the organic chloride are then filtered off. The solvent is removed by distillation.

5.3 g of a viscous substance (90.5% of theory, based on the silicic acid silyl ester employed) are obtained. The GPC diagram shows a uniform compound. The ¹H- and ²⁹Si-NMR data correspond to the following empirical composition:



Example 13

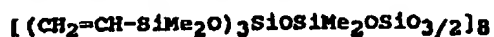
Reaction of octa(dimethylsiloxy)octasilsesquioxane (HSiMe₂OSiO_{3/2})₈ with allyl chloride/palladium and tris(vinyldimethylsilyloxy)hydroxysilane.

2.5 ml of allyl chloride (30 mmol) are added dropwise, under nitrogen as an inert gas, to a well-stirred mixture of 2.5 g of octa(dimethylsiloxy)octasilsesquioxane (20 mmol of Si as the Q unit or as the M^H unit), 0.05 g of palladium (on active charcoal, 5%) and 8 ml of toluene at a temperature of 95°C and the mixture is stirred for 4 hours.

After cooling to room temperature, the reaction mixture is added, under an inert gas, to a well-stirred mixture of 7 g of tris(vinyldimethylsilyloxy)hydroxysilane (20 mmol of Si as the Q^{OH} unit), 3.1 ml of triethylamine (22 mmol) and 25 ml of toluene at a temperature of 50°C and the mixture is stirred for 1 hours.

The catalyst and the organic chloride are then filtered off. The solvent is removed by distillation.

8.5 g of a viscous substance (90% of theory, based on the silicic acid silyl ester employed) are obtained. The GPC diagram shows a uniform compound. The ^1H - and ^{29}Si -NMR data correspond to the following empirical composition:



Example 14

Reaction of octa(dimethylsiloxy)octasilsesquioxane ($\text{HSiMe}_2\text{OSiO}_3/2$)₈ with H_2O , palladium and trimethylchlorosilane.

2.5 ml of octa(dimethylsiloxy)octasilsesquioxane (20 mmol of Si as the Q unit or as the M^{H} unit), 0.05 g of palladium (on active charcoal, 5%) 0.47 ml of water and 11.1 ml of acetone are heated under reflux for 1 hour, while stirring.

After cooling to room temperature, the reaction mixture is added, simultaneously with 4.1 ml of triethylamine (29 mmol) in 10 ml of toluene, to 3.3 ml of trimethylchlorosilane (26 mmol of Si as the M^{Cl} unit) in 20 ml of toluene at room temperature and the mixture is stirred for 10 minutes.

The catalyst and the organic chloride are then filtered off. The solvent is removed by distillation.

4.0 g of a viscous substance (93.5% of theory, based on the silicic acid silyl ester employed) are obtained. The GPC diagram shows a uniform compound. The ^1H - and ^{29}Si -NMR data

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correspond to the following empirical composition:



Example 15

Reaction of octa(dimethylsiloxy)octasilsesquioxane

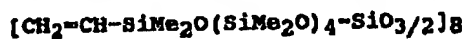
5 $(\text{HSiMe}_2\text{OSiO}_3/2)_8$ with H_2O , palladium and 1-chloro-7-vinyl-octamethyltetrasiloxane

10 2.5 ml of octa(dimethylsiloxy)octasilsesquioxane (20 mmol of Si as the Q unit or as the M^{H} unit), 0.05 g of palladium (on active charcoal, 5%) 0.47 ml of water and 11.1 ml of acetone are heated under reflux for 1 hour, while stirring.

15 After cooling to room temperature, the reaction mixture is added, simultaneously with 4.1 ml of triethylamine (29 mmol) in 10 ml of toluene, to 11 ml of 1-chloro-7-vinyl-octamethyltetrasiloxane (26 mmol of Si as the D^{Cl} unit) in 20 ml of toluene at room temperature and the mixture is stirred for 10 minutes.

The catalyst and the organic chloride are then filtered off. The solvent is removed by distillation.

20 8.2 g of a viscous substance (91% of theory, based on the silicic acid silyl ester employed) are obtained. The GPC diagram shows a uniform compound. The ^1H - and ^{29}Si -NMR data correspond to the following empirical composition:



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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE
PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An organosilicon compound of the formula



in which

z is 4, 6, 8, 10, 12 or 14,

R can be identical or different and represents a hydrogen atom, an organic radical or radicals of the formula



in which

R^1 can be identical or different and represents a hydrogen atom, an organic radical or an organosilicon radical,

R^2 can be identical or different and represents a hydrogen atom or an organic radical and

n is 0 or an integer,

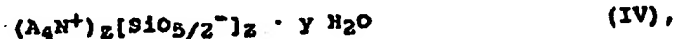
with the proviso that the organosilicon compound of formula (I) contains at least one radical R of formula (II) where $n > 0$.

2. An organosilicon compound as claimed in claim 1, in which R represents a radical of formula (II).

3. An organosilicon compound as claimed in claim 1, in which z is 6, 8 or 10.

4. An organosilicon compound as claimed in claim 1, in which n is an integer from 1 to 20.

5. A process for the preparation of an organosilicon compound as claimed in claim 1, which comprises reacting a cage-like silicate of the formula

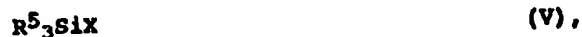


in which

y is a number between 50 and 300,

z is the same as in formula (I) and

A can be identical or different and represents an alkyl radical, with at least one compound (A) of the formula



and/or a hydrolyzate or condensate thereof, in which

R⁵ can be identical or different and is the same as R² above and

X represents a hydroxyl group, an organyloxy radical or a halogen atom,

and at least one organosilicon compound (B) chosen from the group consisting of cyclic organopolysiloxanes of the formula



in which

R⁶ can be identical or different and is the same as R² above and

x represents 3 to 10, silanes of the formula



and/or partial hydrolyzates or condensates thereof, in which

R⁷ can be identical or different and is the same as R² above.

and

D can be identical or different and is the same as X, and organopolysiloxane of the formula



in which

R⁸ can be identical or different and is the same as R² above,

a can be identical or different and represents 0 or 1,

p is 1 to 1,000, and
 x can be identical or different and is the same as x
 above.

6. The process as claimed in claim 5, wherein a silane of
 formula (XII) is employed as component (B).
 7. A process for the preparation of an organosilicon compound as
 claimed in claim 1, which comprises reacting an organosilicon
 compound of the formula



in which

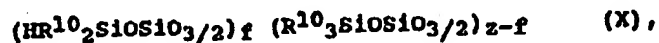
R^9 can be identical or different and is the same as R^2 and
 and

z is the same as in formula (I),

with at least one organosilicon compound (B) chosen from the
 group comprising compounds of formulas (VI), (VII) and (VIII)
 and optionally at least one compound (A) of formula (V)
 and/or a hydrolyzate or condensate thereof.

8. The process as claimed in claim 7, wherein a compound of
 formula (VIII) is employed as component (B).

9. A process for the preparation of an organosilicon compound as
 claimed in claim 1, which comprises reacting an organosili-
 con compound of the formula



in which

R^{10} can be identical or different and is the same as R^2
 above,

z is the same as in formula (I) and

f represents an integer from 1 to z,

with allyl chloride in the presence of platinum metals and/or
 a compound thereof in a first stage to give the corresponding

chlorine compound of the formula



in which R^{10} , f and z are the same as mentioned above, and then reacting compound of formula (X') in a second stage with at least one organosilicon compound (C) chosen from the group consisting of silanes of the formula



in which

R^{11} can be identical or different and is the same as R^2 above,

organopolysiloxanes of the formula



in which

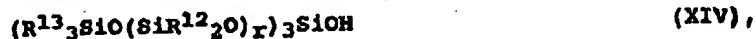
R^{12} can be identical or different and is the same as R^2 above and

r represents 0 or an integer from 1 to 10, organopolysiloxanes of the formula



in which

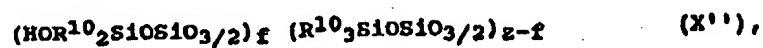
R^{12} and r are the same as above and organopolysiloxanes of the formula



in which

R^{12} and r are the same as above.

10. A process for the preparation of an organosilicon compound of formula (I) which comprises reacting an organosilicon compound of formula (X) with water in a first stage in the presence of a platinum metal and/or compound thereof to give the corresponding hydroxy compound of the formula



in which

R^{10} , f and z are the same as above, and then reacting compounds of formula (X'') in a second stage with at least one organosilicon compound (C) chosen from the group consisting of silanes of the formula



in which

R^{11} can be identical or different and is the same as R^2 above,

organopolysiloxanes of the formula



in which

R^{12} can be identical or different and is the same as R^2 above and

r represents 0 or an integer from 1 to 10,

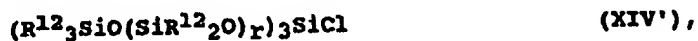
organopolysiloxanes of formula



in which

R^{12} and r are the same as above, and

organopolysiloxanes of the formula



in which

R^{12} and r are the same as above.